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Rice Husk for Photocatalytic Composite Material Fabrication

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Abstract

As a semiconductor, zinc oxide (ZnO) has better UV absorbing properties compared to other semiconductor materials, and therefore, it has better dye degrading abilities. However, ZnO tends to agglomerate, which lead to poor degradation compared to the other semiconductors. In this study, to overcome the agglomeration of ZnO, silica (SiO₂) was combined with ZnO. The composite was tested for its photocatalytic activity. The ZnO/SiO₂ photocatalyst was fabricated on a glass plate. In order to investigate the addition of SiO₂ on ZnO, X-ray diffraction (XRD) and scanning electron microscope-energy dispersive X-ray spectroscopy (SEM-EDS) was used. The result of the XRD analysis demonstrates similar peak results with ZnO XRD data from ICSD 157132 with a hexagonal structure. The results indicate that the ZnO structure did not change after the addition of SiO₂, while SEM-EDS results showed that SiO₂ was supported on ZnO with 8% composition. The optimal composition was found to be ZnO/SiO₂ 95/5, as indicated by high degradation activity, which can degrade up to 89% methylene blue.

Keywords: rice husk, silica, photocatalysis, ZnO, methylene blue

1. Introduction

The textile industry is developing at a rapid pace, and this has a positive impact on garments development. However, it also increases the negative impact through their industrial waste, especially textile dye. One of the means to degrade dye is by the use of a semiconductor material that has photocatalytic activity [1]. Utilization of semiconductors in photocatalysis is an interesting topic, attributable to its ability to degrade compounds with ultraviolet light facilitation [2].

TiO₂ is usually used as a photocatalyst because it is stable compared to the other photocatalytic agents. However, TiO₂ absorbs less UV light compared to ZnO. Therefore, ZnO can degrade more dye. However, in reality, ZnO degrades less dye compared to TiO₂, since ZnO tends to agglomerate [3]. To overcome this problem, SiO₂ can be added to ZnO. Pure ZnO degrades 40% dye in 60 minutes. However, when SiO₂ was added, the degradation increased and showed better results compared to pure ZnO. The addition of SiO₂ to ZnO achieved optimum photocatalytic activity at ZnO/SiO₂ 90/10 weight ratio with 99% dye degradation efficiency [4].

Rice husk is composed of about 20% paddy grain [5]. It is composed of mainly cellulose (~32%), silica (~22%) and lignin (~16%) [6]. After milling, rice husk becomes a major waste product, and is not utilized optimally. In 2015, Indonesia produced 75 million tonnes of rice (Central Agency on Statistics, bps.go.id), and therefore, rice husk becomes abundant and a cheap source for silica.

The efficiency of degradation and decolourization is affected by the stability of ZnO layer and ZnO layer morphology. An experiment was conducted by fabricating ZnO/SiO₂ composite with 95/5, 90/10, and 85/15 weight ratio. The results indicated good results when the composite was used to degrade methylene blue with synthetic SiO₂ made from rice husk as the supporting material. Therefore, the present study aims to fabricate ZnO/SiO₂ with less agglomeration [4].

2. Experimental section

2.1. Isolation of SiO₂

Rice husk was carbonated at 400°C for 6 hours, followed by increasing the heat to 700°C in an argon atmosphere for 4 hours. The carbon was then ground and seized using a 100 mesh sieve. The carbon was suspended in with a mole ratio 1/3/150 = silica:potassium carbonate: water and refluxed for 150 minutes. The mixture was filtered and the filtrate was allowed to cool. The SiO₂ was precipitated and collected after filtering the solution.

2.2. Fabrication of ZnO/SiO₂ nanocomposite

Three weight ratio of ZnO/SiO₂, namely, 100/0, 95/5, 90/10 and 85/15, were prepared to give 3 g of total mass. The solid mixture was then suspended in 100 mL of distilled water. The suspension was stirred using a magnetic stirrer (500 rpm) for 2 hours, followed by sonication for 90 minutes (Elma ultrasonic LC 30H). The ZnO/SiO₂ suspension was dropped onto a glass slide (1 × 3 cm) with a pipette until the entire glass surface was covered. The slide was dried at 40°C for 12 hours, followed by calcinations at 450°C for 1 hour. The slide was washed using distilled water, and the layer was characterized using X-ray diffraction (XRD) and scanning electron microscope-energy dispersive X-ray spectroscopy (SEM-EDS).

2.3. Determination of maximum wavelength and standard curve

The absorbance of 1 ppm methylene blue solution was recorded at 500–700 nm in wavelength. The wavelength at which the highest absorbance was detected was used to measure the concentration of methylene blue. The standard curve was made by measuring the absorbance of

methylene blue solutions with concentration values of 0.2, 0.4, 0.6 and 0.8 ppm. The absorbance was plotted against concentration, and used as a standard curve.

2.4. Photocatalytic assay

For photocatalytic assay, a glass slide with ZnO/SiO₂ layer was inserted into 50 mL of 1 ppm methylene blue in a test tube. It was followed by irradiation using a mercury lamp for 4 hours. Every 2 hours, 2 mL of sample was collected, and its methylene blue content was determined using a visible spectrophotometer at 660 nm. The assay was performed for all the fabricated slides.

3. Results and discussions

3.1. ZnO/SiO₂ photocatalyst

The ZnO/SiO₂ photocatalyst was fabricated to give final mass of 3 g with 95/5, 90/10, 85/15 weight ratio, as described in previous studies [4, 7]. The fabrication was conducted in distilled water, while assay was performed in two different solvents, i.e., distilled water and methanol. According to the assay results, both solvents yielded the same ZnO attachment level on the glass slide. Therefore, both water and methanol are effective as solvents, as previously proposed [7]. In order for ZnO and SiO₂ to completely disperse in water, the suspension was stirred with a magnetic stirrer at 500 rpm for 2 hours, as recommended by prior work [4].

Sonication with ~30 kHz for 90 minutes was conducted to homogenize the ZnO/SiO₂ so that no agglomeration occurs. Prior to the coating, the glass slide was cleaned using acetone to remove impurities that can interfere with the attachment of ZnO/SiO₂. The glass slide that was coated with ZnO/SiO₂ was dried in a 40°C oven for 12 hours to remove excess water so that the ZnO/SiO₂ attaches strongly onto the glass slide (**Figure 1**).

To increase the attachment of ZnO/SiO₂ onto the glass slide, it was heated to 450°C. The surface where ZnO/SiO₂ is attached should be a flat surface, so that when the surface is washed it is easier for the agglomerated ZnO/SiO₂ to be washed [4].

3.2. Characterization results

SEM-EDS and XRD was performed to investigate the ZnO coating onto glass slides. Complete analysis was performed for ZnO/SiO₂ 95/5 weight ratio. The result of SEM is illustrated in **Figure 2**. It can be observed on the 500× magnification that the ZnO/SiO₂ layer attached uniformly with low porosity. A porous structure started to appear at 1000× magnification. The particles attachment affects the efficiency of methylene blue degradation, since it determines hydroxyl radical generation by ZnO to degrade the dye.

Figure 3 shows the ZnO layer without SiO₂ addition. It appears that the particles do not attach uniformly, and have a higher porosity compared to the ZnO/SiO₂ layer, as shown in **Figure 2**. It appears that the addition of SiO₂ to ZnO is significantly effective to facilitate a uniform spread

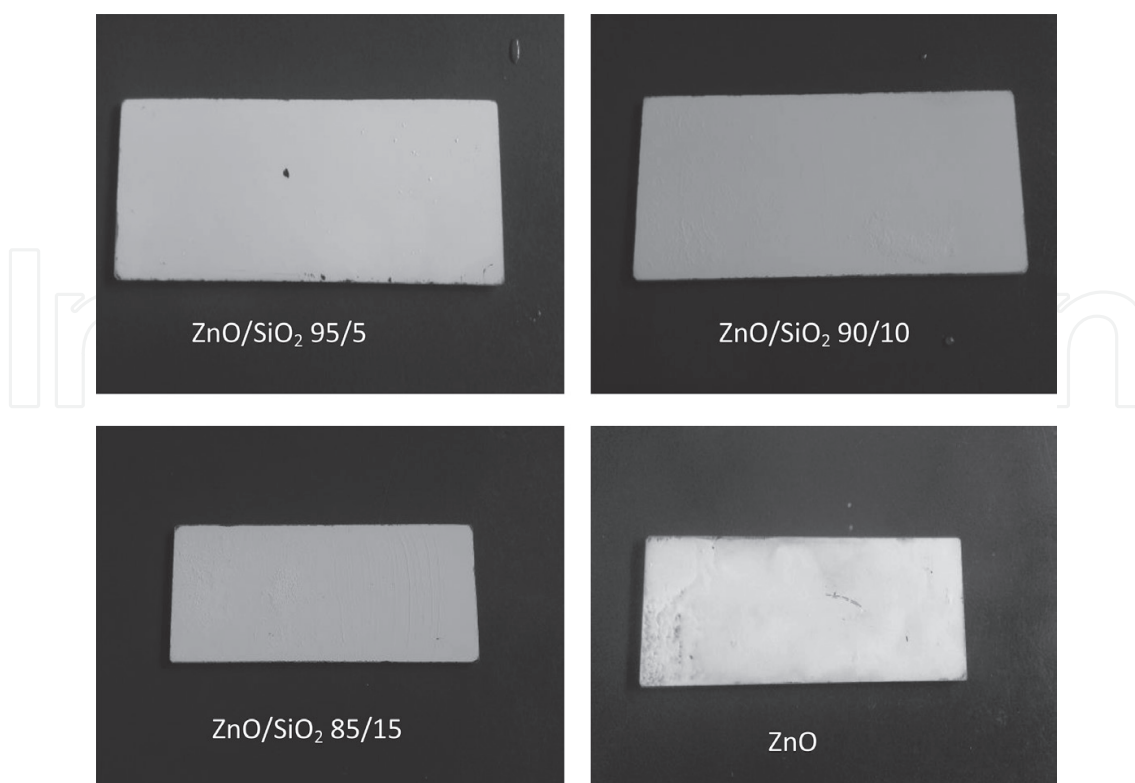


Figure 1. ZnO/SiO₂ and ZnO.

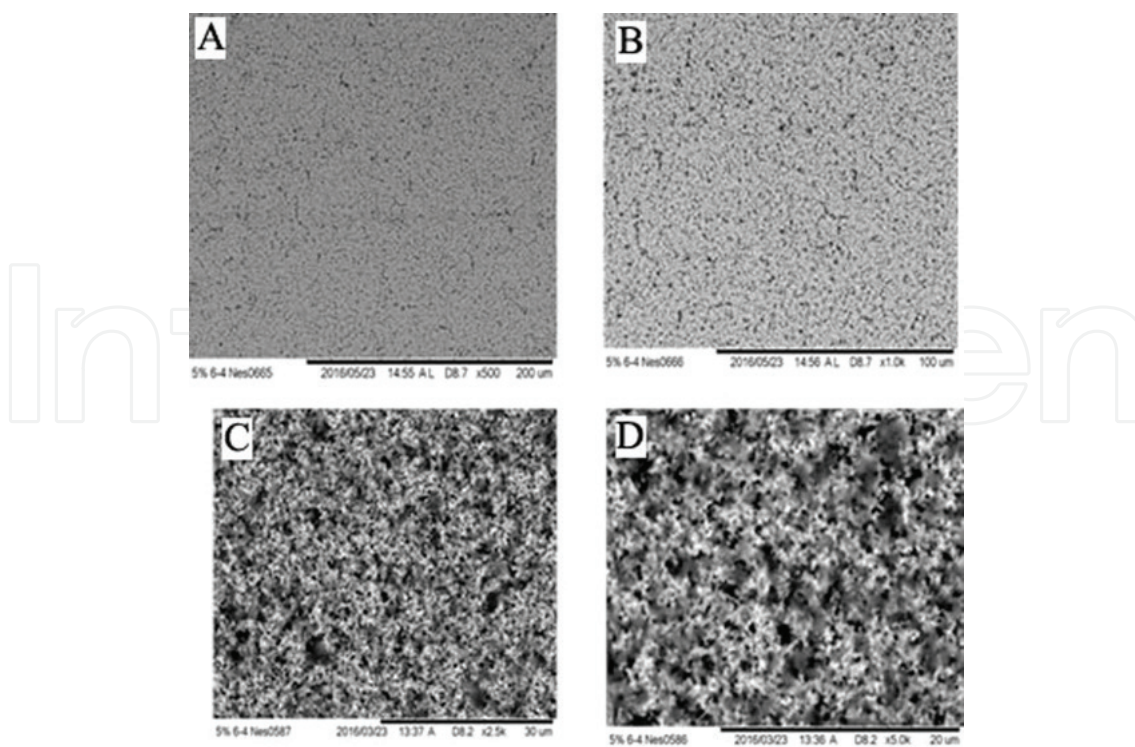


Figure 2. Micrograph of ZnO/SiO₂ at 95/5 weight ratio at (A) 500-, (B) 1000-, (C) 2500-, and (D) 5000-fold magnification.

of ZnO when attached onto the glass slide surface, which can then reduce the porosity of the ZnO/SiO₂ layer. A lower porosity leads to a higher ZnO attached to the glass slide, which acts as a hydroxyl radical generator. Based on the comparison results of ZnO to ZnO/SiO₂ with 95/5 weight ratio, it is clear that the composite can produce more hydroxyl radical, which leads to a more effective dye degradation.

The EDS results are presented in **Figure 4**. EDS is used to investigate the composition of ZnO and SiO₂ in ZnO/SiO₂ mixture. With 95/5 weight ratio, Zn and Si composition was 61.64 and 8.38% weight respectively. However, according to the calculation results, the composition of Zn and Si should be 76.23 and 2.30% weight respectively. A higher Si composition and a lower Zn composition compared to the theoretical value is due to the ZnO being carried

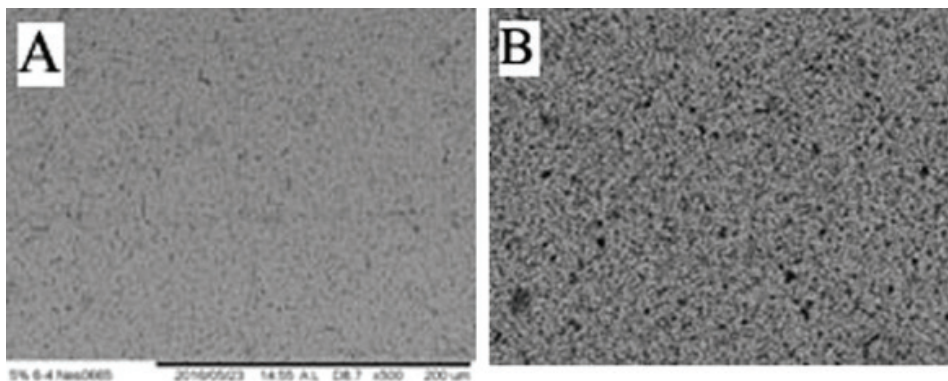


Figure 3. Micrograph of (A) ZnO/SiO₂ 95/5 weight ratio and (B) ZnO with 500× magnification.

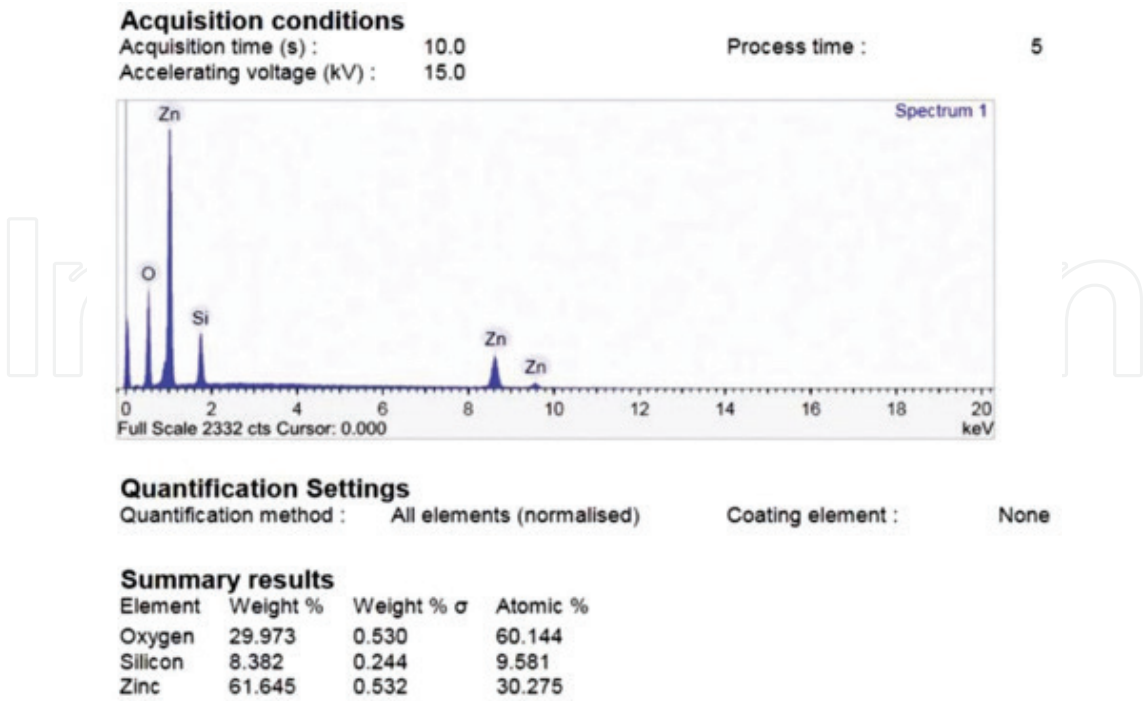


Figure 4. EDS results of ZnO/SiO₂ 95/5 weight ratio.

away during the washing process, especially the agglomerated ZnO. The agglomeration may occur when sonication is extensively long. When more ZnO is washed away, a more porous structure occurs on the layer (**Figure 3**). A high porosity on the layer reduces the ability of ZnO to form hydroxyl radical, which then reduces the rate of degradation. From the EDS results (**Figure 3**), it was proven that 8.38% of SiO₂ is supported on the ZnO particles. It was also found that around 1.22% weight was not detected by the EDS method, which indicates the presence of impurities in the layer.

To investigate the effect of SiO₂ on the ZnO structure, XRD was used. The result of XRD is presented in **Figure 5**. It was found that peaks at 32.33°, 34.67° and 36.85° of ZnO/SiO₂ was shifted compared to standard ZnO. This shift occurred as a result of the SiO₂ attachment on ZnO. The intensity of the peaks indicates that there is no difference between peaks of ZnO/SiO₂ compared to standard ZnO (ICSD 157132 standard), which has a hexagonal crystal structure. This result is in agreement with previously published results, which describe that layers of ZnO have a hexagonal structure.

The results indicate that the addition of SiO₂ does not change the ZnO crystal structure. However, the addition of SiO₂ can increase the distribution of ZnO on the glass slide, thus resulting in a more homogen layer, which leads to no agglomeration. The XRD of ZnO/SiO₂ shows that the SiO₂ peak appears with very low intensity at $2\theta = 20\text{--}25^\circ$ (**Figure 5**). The low intensity peak appears because the SiO₂ amount in ZnO/SiO₂ was low, i.e. 5%. The peak at $2\theta = 23.5^\circ$ with low intensity belongs to SiO₂ from rice husk with an amorphous property.

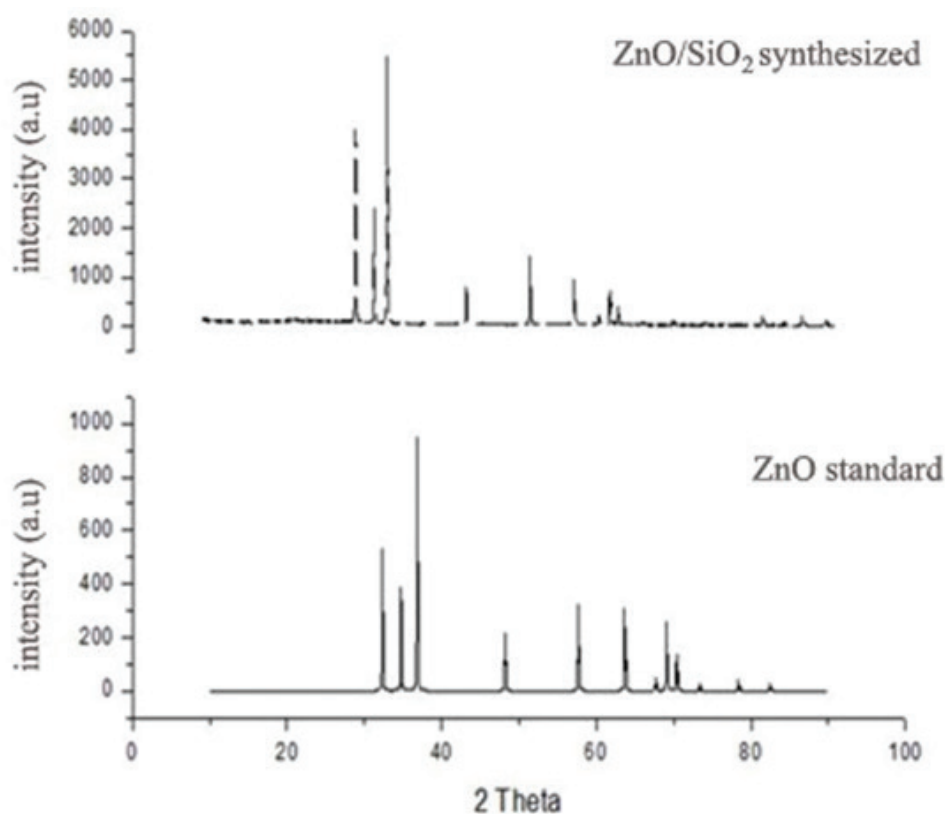


Figure 5. XRD of ZnO/SiO₂ and ZnO standard (ICSD 157132).

This result confirmed that SiO_2 used to fabricate ZnO/SiO_2 is SiO_2 from rice husk with an amorphous property (**Figure 6**).

3.3. Maximum wavelength and standard curve of methylene blue

The wavelength at which maximum absorbance of methylene blue was detected is 660 nm. The maximum wavelength has the highest sensitivity, and therefore the measurement of methylene blue concentration was conducted at this wavelength to the minimize error rate. The correlation of the standard curve was 0.9909, which shows that the method has good correlation.

3.4. Photocatalysis assay

In the photocatalysis assay, samples were collected four times every hour, and the concentration of methylene blue was determined by measuring the absorbance of the samples and converted to a concentration using a standard curve. The percentage of the efficiency of methylene blue degradation was obtained by comparing the concentration of methylene blue before and after radiation. The efficiency of degradation is presented in **Figure 7**.

As shown in **Figure 7**, after 1 hour of radiation, ZnO/SiO_2 with 95/5 weight ratio was more effective compared to the other samples, as it can degrade up to 52.5% of methylene blue. After 3 hours of irradiation, ZnO/SiO_2 with 90/10 weight ratio degrades the dye better compared to the other samples. After 4 hours of irradiation, ZnO/SiO_2 photocatalysts with weight ratio of 95/5, 90/10 and 85/15 showed 89.95, 82.57 and 37.40% degradation percentage respectively. The photocatalysts with 95/5 and 90/10 weight ratio is more effective in degrading methylene blue dye compared to 85/15 weight ratio, as indicated by percentage degradation above 80%. When SiO_2 was used by more than 10%, the ability of the photocatalysts became lower. This is likely caused by SiO_2 covering ZnO that should be act as photocatalysts, which leads to a lower hydroxyl radical formation. ZnO/SiO_2 photocatalysts with 85/15 weight ratio

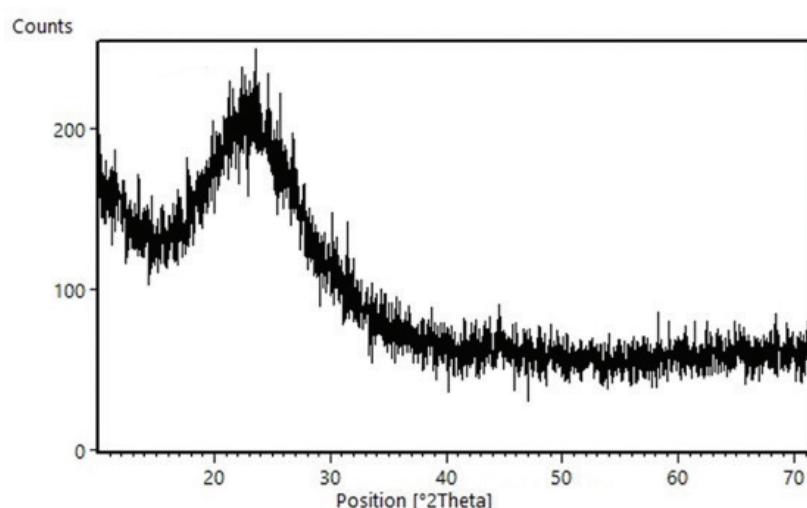


Figure 6. XRD of SiO_2 .

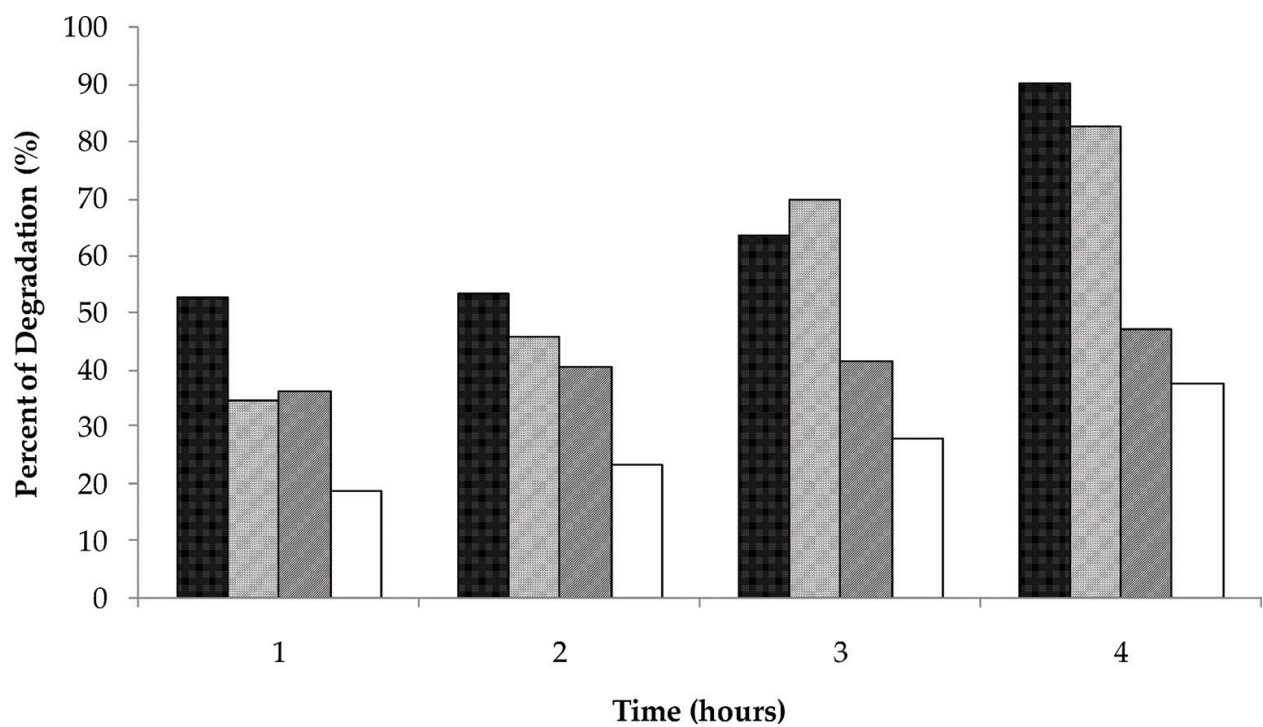


Figure 7. Efficiency of methylene blue degradation using ZnO/SiO₂ photocatalysis with various ZnO/SiO₂ weight ratio. Irradiation time was 4 hours.

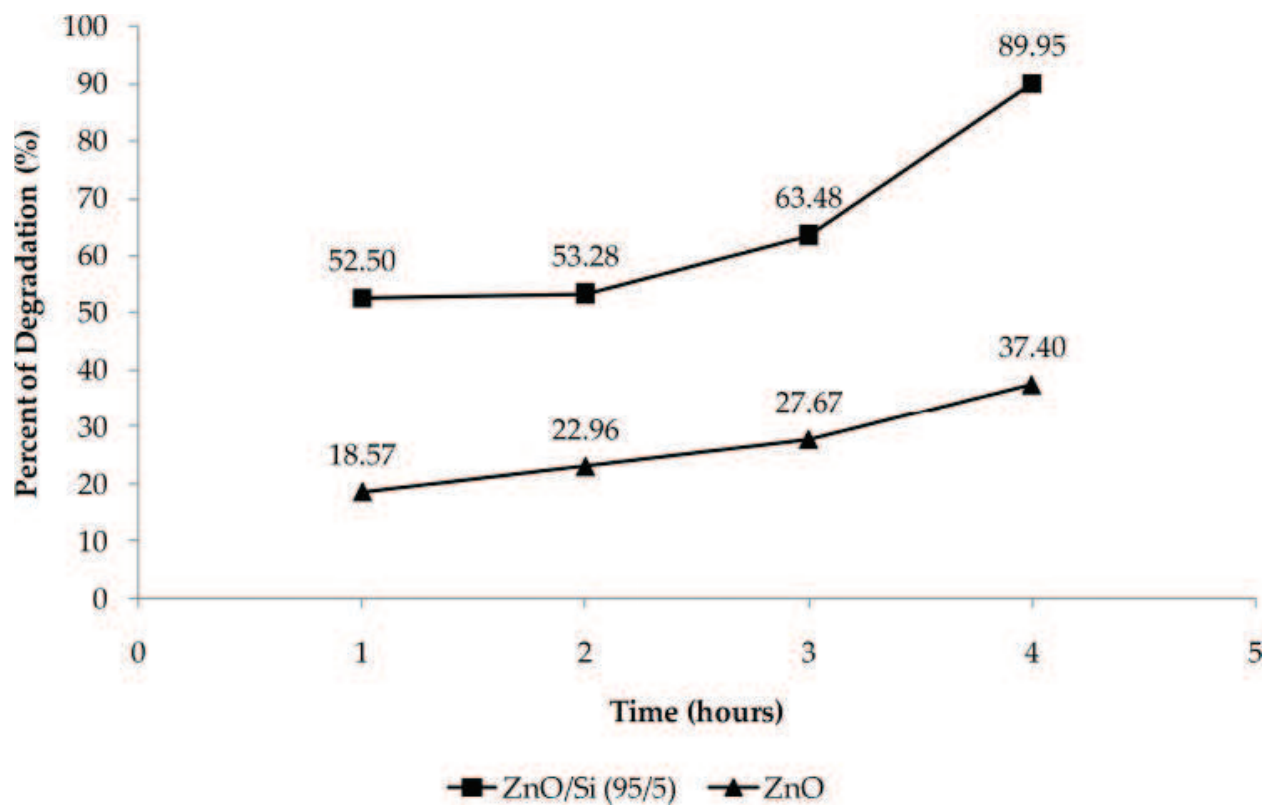


Figure 8. Comparison of methylene blue degradation efficiency using ZnO/SiO₂ compared to ZnO photocatalyst.

less efficient because SiO_2 is not a semiconductor material, so it cannot produce free electrons and hydroxyl radicals. According to Behnajady et al. [8], less hydroxyl radicals will lead to a lower dye reduction efficiency. **Figure 7** confirms this, where photocatalysts with 95/5 weight ratio showed the highest dye degradation.

Figure 8 shows the comparison between ZnO/SiO_2 and ZnO photocatalytic activity. It is clear that the addition of SiO_2 increases the effectiveness of the photocatalyst, as indicated by higher methylene blue degradation of up to 89.95%, while ZnO without SiO_2 can only degrade 37.40%. According to Soltani et al. (2015), this is caused because the ZnO attachment without SiO_2 was not uniform on the glass slide surface that tends to form a porous structure. The addition of SiO_2 to ZnO assisted the attachment to form a uniform layer, and this leads to lower porosity.

4. Conclusion

The addition of silica from rice husk to ZnO photocatalysts improves the spread of the particles uniformly on the glass slide. The addition of the silica does not alter the crystal structure of the ZnO . The optimal composition was found to be ZnO/SiO_2 95/5, as indicated by a high degradation activity, which can degrade up to 89% methylene blue.

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References

- [1] Selvam K, Swaminathan K, Chae K-S. Decolourization of azo dyes and a dye industry effluent by a white rot fungus *Thelephora* sp. *Bioresource Technology*. 2003;**88**:115-119
- [2] Dijkstra MF, Buwalda H, de Jong AWF, Michorius A, Winkelman JGM, Beenackers AACM. Experimental comparison of three reactor designs for photocatalytic water purification. *Chemical Engineering Science*. 2001;**56**:547-555
- [3] Behnajady MA, Moghaddam SG, Modirshahla N, Shokri M. Investigation of the effect of heat attachment method parameters at photocatalytic activity of immobilized ZnO nanoparticles on glass plate. *Desalination*. 2009;**249**:1371-1376

- [4] Soltani RD, Shams Khoramabadi G, Godini H, Noorimotlagh Z. The application of ZnO/SiO₂ nanocomposite for the photocatalytic degradation of a textile dye in aqueous solutions in comparison with pure ZnO nanoparticles. *Desalination and Water Treatment*. 2015;**56**:2551-2558
- [5] Madrid R, Nogueira CA, Margarindo F. Production and characterization of amorphous silica from rice husk waste. In: *The 4th International Conference on Engineering for Waste and Biomass Valorisation*; 10-13 September 2012; Porto, Portugal; 2012
- [6] Prasad R, Pandey M. Rice husk ash as a renewable source for the production of value added silica gel and its application: An overview. *Bulletin of Chemical Reaction Engineering & Catalysis*. 2012;**7**(1):1-25
- [7] Behnajady MA, Modirshahla N. Photooxidative degradation of Malachite Green (MG) by UV/H₂O₂: Influence of operational parameters and kinetic modeling. *Dyes and Pigments*. 2006;**70**:54-59
- [8] Behnajady MA, Modirshahla N, Daneshvar N, Rabbani M. Photocatalytic degradation of C.I. Acid Red 27 by immobilized ZnO on glass plates in continuous-mode. *Journal of Hazardous Materials*. 2007;**140**:257-263